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MEMBRANE POTENTIALS

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

JOHN MOUK ORT, B. CHEM. ENG., M. SC.

L. C.

The Ohio State University
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PREFACE

This investigation was carried on during the academic year 1923-24 under the direction of Dr. Wesley G. France, Assistant Professor of Physical Chemistry, to whom the author is indebted not only for the suggestion of the problem but also for his interest in the work and for many suggestions which helped in carrying it out.

The author also gratefully acknowledges the help received from the E. I. duPont de Nemours and Company of Wilmington, Delaware. Their duPont Fellowship in Chemistry made possible the devotion of a year entirely to this research.

Columbus, Ohio, June, 1924.

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MEMBRANE POTENTIALS

Introduction and Historical

When membrane potentials are calculated from thermodynamic equations, the membranes are assumed to be ideal. That is, it is assumed that there is no potential difference between the membrane and its surroundings other than that due to the effect upon which the thermodynamic equation is based. Des Coudres,[1] Donnan,[2] Prideaux,[3] Leob,[4] and others have gathered much experimental data in support of such equations. The agreement between theoretical and experimental results has not always been within the limits of experimental error. For example, Donnan and Allmand, (loc. cit.) say,—"the phenomena are not so simple as supposed in the theory mentioned." Still, at times, the approximation of the observed values to the calculated values has been very close, and it seems difficult to doubt that the theory underlying these calculations is sound.

Many have observed that different membranes or membrane materials crary different electrical charges under the same set of conditions.[5] And it has been further observed that the charge for a given material changes under different conditions and can even be reversed in sign in suitable surroundings.[6] It has also been pointed out that some of the discrepancies between the theoretical values and the values obtained by membrane potential measurements may be due to these charges, which are specific for each membrane under the conditions measured.[7] Apparently there are no published data in which the specific charges of the membranes are considered in the accurate determination of membrane poten-

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[1] Des Coudres, Th.: *Pogg. Ann.*, 46, 292 (1892).

[2] Donnan, F. G., and Harris, A. B.: *J. Chem. Soc.*, 99, 1554 (1911); Donnan, F. G., and Garner, W. E.: *J. Chem. Soc.*, 115, 1313 (1919); Donnan, F. G., and Green, G. M.: *Proc. Roy Soc.*, (A) 90, 450, (1914); Donnan, F. G. and Allmand, A. J.: *J. Chem. Soc.*, 105, 1963, (1914).

[3] Prideaux, E. B. R.: *Trans. Farad. Soc.*, 10, 160, (1914).

[4] Loeb, J., "*Proteins and the Theory of Colloidal Behavior*," Chapter VIII. McGray-Hill Book Co. This book gives a complete resumé and a bibliography of Loeb's numerous publications on this subject.

[5] Perrin, J.: *J. Chim Phys.*, 2, 601 (1904); 3, 50 (1905).
Bartell, F. E., and Hooker, C. D.: *J. Am. Chem. Soc.*, 38, 1029 (1916).
Coehn, A., and Franken J.: *Ann Physik*, 48, 1005, (1915-16).

[6] Perrin: loc. cit.
Bartell and Hooker: loc. cit.
Coehn and Franken: loc. cit.

[7] Donnan and Allmand, Loc. cit.; Prideaux; loc. cit.
Bartell and Hooker loc. cit.

tials. In the present investigation these charges have been considered in the measurement of one type of membrane potential. The data obtained indicate that there are two potential effects involved, one, the specific membrane potential due to the nature of the membrane and electrolyte, and the other the Des Coudres effect. In other words, what we really measure as the potential difference across a membrane is the algebraic sum of these two effects. One potential difference is constant under constant conditions; the other varies according to the thermodynamic equation.

The particular effect chosen for study was first described by Des Coudres (loc. cit.). This kind of a membrane potential is produced by the pressure of a column of mercury resting on a membrane impermeable to liquid mercury, but permeable to Hg^+ ions, to the water, and to the other ions of the electrolyte in contact with the opposite side of the membrane. By this pressure Hg^+ ions are forced through the membrane leaving the liquid mercury charged negatively. Because of electrostatic attraction equilibrium in this passage of Hg^+ ions through the membrane is reached when the work which would be necessary to force a gram equivalent of Hg^+ ions away from the negatively charged liquid mercury is just equal to the work which would be necessary to raise the weight of the gram equivalent of ions through a distance equal to the height of the mercury column above the membrane. Hence, the potential difference as read across an ideal membrane, should, as Des Coudres derived it, be given by the equation:

$$E = \frac{Q \times 10^{-1}}{S} \text{ volts,}$$

in which E = the membrane potential per each atmosphere of pressure of the liquid mercury column, Q = the electrochemical equivalent of the Hg+ ion, and S = the density of the liquid mercury in the pressure column. This amounts to very nearly 1 microvolt per height of 5 cms.

Des Coudres used parchment paper membranes. While some experiments were made with parchment paper, and also with gold beaters' skin, the data given in this dissertation was gathered only from collodion membranes. Des Coudres obtained results which checked his equation only approximately. His discrepancies ranged from 3% to 20%, growing larger at the higher pressures and potentials, and were probably due somewhat to polarization. The highest pressure he used was 113 cms. of mercury. He attributed these differences to errors in his potential measurements. The data in

this dissertation also show that the measured membrane potentials are not in agreement with those calculated. Indeed, they are often many times the calculated values, and sometimes opposite in sign. However, after the specific charge on the membrane becomes constant, then the measured additional charges, which are due to the pressure effect, agree with the calculated additions within the limits of error of the potential measurements.

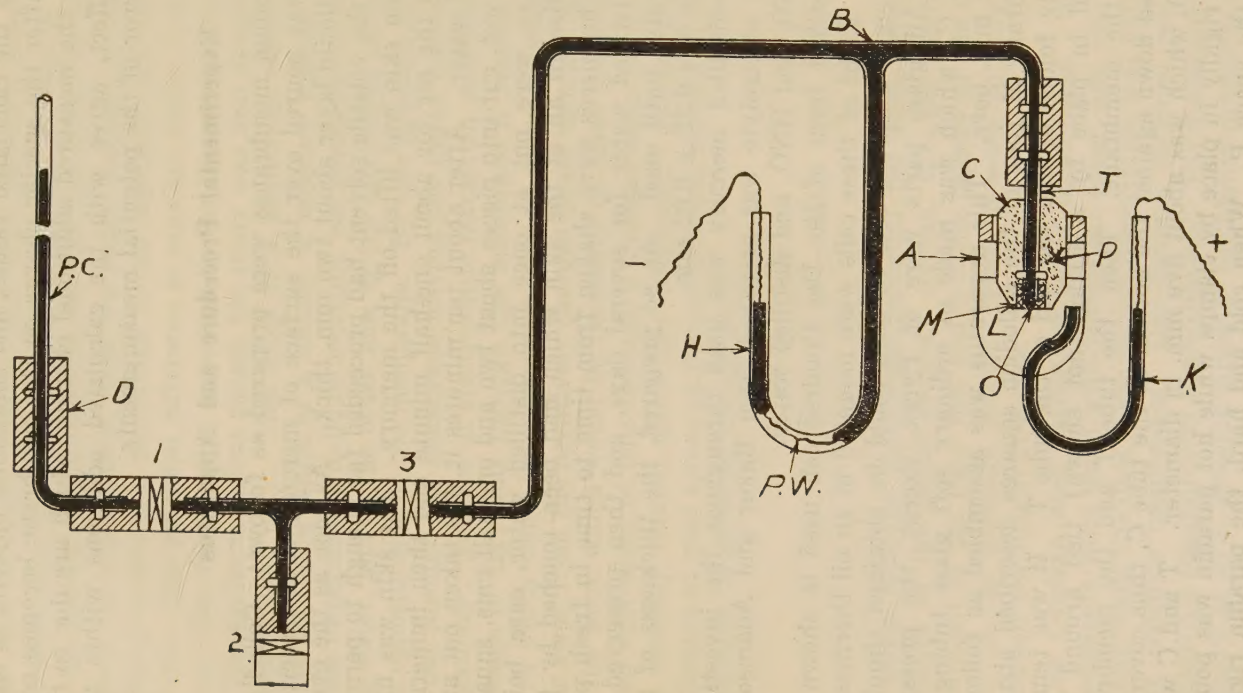
Experimental Procedure and Apparatus

The collodion membranes were prepared as follows: Collodion, U. S. P., was poured over the surface of mercury in a casserole, forming a liquid layer about two mm. thick. As soon as the evaporation of the volatile solvent had proceeded far enough to permit, the collodion skin was lifted off the mercury. The skin was first exposed to the air for about one-half minute and then immersed in distilled water. After about ten minutes it was taken out and, while still wet, cut into pieces about two and one-half cms. square. These pieces were put at once into distilled water, care being taken to discard all of the skin which had been touched by the fingers. The pieces were shaken from time to time in fresh portions of distilled water for several days, and then preserved in distilled water until used. As so prepared, the thickness of the membranes was 0.22 ± 0.02 mm.

Pure, redistilled mercury was used throughout the investigation. The electrolyte was prepared from Baker and Adamson's C. P. $HgNO_3$ and HNO_3 and distilled water.

The modified form of the Des Coudres cell used is shown in Figure I. Eight of these cells were mounted in an oil thermostat and thus eight different sets of data could be obtained simultaneously. All glass parts were of Pyrex, except the pressure column P. C., which was made of ordinary soft glass tubing of about five mm. bore. This apparatus was assembled as follows: The membrane M (one of the collodion squares described above) was tightly folded around the end of the tube T. It was temporarily held in place by a string (not shown) tied around the edges of the membrane. Then the tube T and the membrane were forced down against the bottom of the tube C, thus covering the hole O, which was about five mm. in diameter. T and C were then held rigidly in place by clamps while hot paraffin was poured in, filling the space P. When cold and hard, the paraffin rigidly held these two tubes in place and as a unit they were then placed at the end of the tube B, as shown. T was then fastened to B by

FIG. 1.



heavy rubber pressure tubing around which was then wound iron wire. The tubes B and T were about five mm. bore. T was ten cms. long; C was six cms, long, and two cms. in diameter at the middle.

The U-shaped tube H, through the sealed-in platinum wire P. W., furnished electrical connection with the mercury side of the membrane. The tube B was connected to the pressure column P. C. by means of the T-tube and rubber connections shown to the right of D. The screw clamps, marked 1, 2, and 3, served to regulate the height of mercury in P.C. and thus the pressure on M, which is given by the height of mercury in P.C. above the level of the membrane M. The whole apparatus to the right of D was mounted on a metal frame and could be carried about as a unit.

The membrane cell A was five cms. in diameter and ten cms. long. The rubber stopper in A fitted the tube C loosely and, in the space between, loosely packed cotton prevented practically all evaporation and yet kept the inside always at atmospheric pressure. The side tube K furnished electrical contact with the electrolyte L which bathed the under side of the membrane.

The membrane M and both electrical contacts at H and K were beneath the level of the oil in the thermostat. Hence, all metallic thermo-electric effects were eliminated. All contact E. M. F.s were eliminated at metal junctions by having such junctions in opposing pairs. Reversal of the leads showed that this was actually accomplished.

All potentials were measured on a White Double Potentiometer, manufactured by the Leeds and Northup Company and were read to the nearest microvolt. The ordinary Weston Standard Cell was used as the standard E. M. F. The oil thermostat was kept at constant temperature to $\pm 0.01^\circ$ C.

The experiments were performed according to the following procedure: The oil thermostat was adjusted to hold the temperature at 25° C., and the eight cells were mounted in it as described above. Some of the membranes were freshly mounted and only brought into contact with the electrolyte just before they were placed in the thermostat. Others had been previously mounted in the tube C, Figure I, and had stood for over two weeks in contact with the electrolyte used. The former were to show the effect of time on the charge; the latter were to show the final equilibrium charge, and to furnish data on the pressure effect.

The pressure effect was investigated at the same time as the data on the time effect was gathered. To do this, mercury was poured into the top of the pressure column P.C., Figure I, or allowed to run

out at screw clamp 2, according to whether it was desired to raise or lower the pressure of the membrane. The potentiometer readings, which were made between the pressure changes, showed that the membrane potentials usually responded to these pressure changes before they could be read.

After the freshly mounted membranes had come to equilibrium at 25° C., and all the desired data at this temperature were gathered, the thermostat was then adjusted for another temperature. After the cells had reached equilibrium at the new temperature, still another temperature was tried, etc. Finally, the thermostat was again set at 25° C., the first data at this temperature checked, and the run stopped. This whole procedure was then repeated for different electrolytes.

The Pressure Effect

In presenting data on the pressure effect and in the discussion immediately following, the cause of the specific charge is ignored. That subject will be taken up later in the dissertation. Since the specific charge is additive to the pressure effect, when attempting to measure the pressure effect it was only to be desired that the specific charge remain constant during these measurements. This was never entirely realized. Fluctuations of more than one microvolt during a pressure run were common. Since, however, the response of membrane potential to pressure change is almost instantaneous, while the specific charge varies comparatively much slower, this difficulty is not serious. It only prevents the exact duplication of a reading for a given pressure at different times. Table I gives the results of a typical pressure run.

TABLE I

I	II	III	IV	V
Time in Minutes	Pressure in cms. Hg.	Observed charge on Pressure side of Membrane Microvolts	Change from Last Reading Observed Microvolts	Calculated Microvolts
0	125	—34	0	0
120	125	—36	—2	0
165	125	—41	—5	0
195	125	—37	+4	0
203	155	—43	—6	—6
209	155	—43	0	0
211	115	—35	+8	+8
217	115	—35	0	0
218	75	—27	+8	+8
263	75	—30	—3	0
265	40	—23	+7	+7
271	40	—23	0	0
272	0	—15	+8	+8
278	0	—15	0	0
280	40	—23	—8	—8
287	40	—22	+1	0
289	75	—29	—7	—7
293	75	—29	0	0
296	150	—45	—16	—15
301	150	—44	+1	0
302	0	—14	+30	+30
327	0	—11	+3	0
335	40	—19	—8	—8

In this table, Column I gives the time in minutes after it was decided to record readings for presentation here. Zero time is therefor an arbitrarily chosen starting point and has nothing to do with the time of starting the run when the membrane was first put into the electrolyte. The time is given to show how quickly the membrane potential responded to a change in pressure. Column II gives the pressure, in excess of atmospheric pressure, that was on the membrane when the readings were taken. Column III gives the actual membrane potential as read. Columns IV and V give the change in membrane potential from the last previous reading. Column IV gives merely the difference between any given reading and the one before it, while Column V gives the differences that should be found, as calculated from Des Coudres' equation. A pressure increase of 5 cms. of mercury should make the membrane potential one microvolt more negative, while a decrease in pressure of the same amount should make the membrane potential one microvolt more positive. The first four readings given in the table show how the specific charge will vary over a period of time when, apparently, it should remain constant.

With all the different electrolytes used, all the membranes, which gave reasonably constant membrane potentials, were charged negatively at 25° C. As the data given later in the dissertation show, cooling the membranes lowers this negative charge. But it was found, probably because of the difference between the coefficients of expansion of paraffin and glass, that this cooling weakened the mounting of the membrane. Therefore, when it was attempted to lower the temperature in order to make a pressure run on a membrane charged positively at zero pressure, it was invariably found that the membranes would not stand much pressure. Hence, it was impossible to get long continued pressure runs on the membranes used, starting with a positive charge. This was desirable in order to show that the pressure effect was exactly additive, either to a negative or to a positive specific charge. However, in several isolated cases where, at a lower temperature, the positive charge on the membrane was only of the order of a few microvolts, it was found possible to reverse this positive charge by increasing the pressure on the membrane. For instance, in one case the membrane potential as read for zero pressure was +7 microvolts. Upon increasing the pressure to 40 cms., the membrane potential was found to be —1 microvolt, exactly as it should have been. But when an attempt was made to continue the run at higher pressure, the mercury broke through the mounting.

The above data seems to support the main contention in this dis-

sertation that the specific charge must be considered when an attempt is made to check theory by the data of membrane potential measurements. It is evident from the table that the thermodynamically calculable effects when added algebraically to the specific charges, determined for zero pressure, give the measured membrane potentials within the limits of accuracy of the potential measurements.

While the conditionss in a Des Coudres cell are admittedly somewhat different from those of a Donnan equilibrium, nevertheless there is this similarity, which is both necessary and sufficient for any membrane potential—the conditions are different on the two sides of the membrane.[8]

It seems quite probable that, in a Donnan equilibrium, the ions to which the membrane is impermeable affect the contact potential difference between the membrane and solution by adsorption on that side to which they are confined. Hence, the contact potential is different on the two sides, and there arises a membrane potential across the membrane which is an effect quite other than that due to the diffusion forces whose values Donnan first calculated,[9] and which Loeb (loc. cit.) considered in his membrane potential measurements. It is quite probable that this specific effect may be so small in some cases, in comparison to the Donnan effect, that it may be ignored. However, as will be shown later, this specific effect is quite variable and, under certain conditions, must be taken into account.

If this is correct, it is evident that Prideaux (loc. cit.) in plotting the data from his membrane potential measurements, should have obtained curves which had intercepts on the potential axis, instead of passing through the origin. This indicated a constant potential algebraically additive to the Donnan effect investigated. In his case, a further correction should be made by the use of activity coefficients, instead of degrees of dissociation. Perhaps, also, if Donnan and his students, and Loeb and his co-workers had known the value of the specific charge and allowed for it in their investigations, their discrepancies, quite small at times, might altogether have vanished.

In the experiments in which gold beaters' skin and parchment paper were used instead of collodion, difficulties were encountered which proved insurmountable. The gold beaters' skin would not stand the pressure and the parchment paper seemed to react chemically with the electrolyte and turn pink after about two days. Only

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[8] For a complete resumé of the conditions of a Donnan equilibrium see: Donnan, F. G.: *Chemical Reviews*, 1, 73 (1924).

[9] Donnan, F. G.: *Z. Electrochem*, 17, 572 (1911).

very erratic results were obtained with these two materials and hence no accurate pressure experiments were possible. Some indication of their tendency in specific charges was noticed and these observations will be mentioned later.

A Specific Charge Hypothesis

An hypothesis to account qualitatively for the specific charges as read in the Des Coudres cell will be presented. However, before doing this it is advisable to consider the nature of collodion membranes and their mounting in the cell used.

Bartell and Van Loo[10] have shown that collodion membranes are, in structure, simply sheets of impervious collodion penetrated by numerous small holes. These holes are formed by the evaporation of the volatile matter in the preparation of the membrane. Regulation of the extent of the evaporation regulates the size of the holes. If the evaporation continues until all the volatile matter is gone, the holes fill up and the membrane becomes impermeable. In this work this was found to be true, for such membranes, when placed in a circuit, made no electrical connection. Hence, all diffusion and ionic conduction take place through these capillary channels.

Bartell and Van Loo (loc. cit.) present data showing the diameters of these holes for membranes ranging from "least permeable" to "very permeable." All diameters are of the order of magnitude of a micron. Since molecules of mercury are much smaller than the pore diameters, it seems reasonable to assume that the impermeability is due to capillary attraction, since mercury is depressed in a capillary tube. We have, then, the picture of a system of countless little tubes with mercury in one end.

Therefore, in the cell shown in Figure 1, what is measured is the potential difference between the large mercury surface at the inside end of the tube K, and the countless little inverted mercury surfaces in the pores of the membrane. Since the large mercury surface is on the same level with the little surfaces, this potential difference should be zero, if the membrane were ideal. But the membrane is not ideal for it is charged. This charge must affect the final equilibrium between the Hg^+ ions and these little surfaces. Hence the charge on these surfaces is not the same as that on the large surface at the inner end of K. The difference between the charges, then, is the specific charge as measured across the membrane.

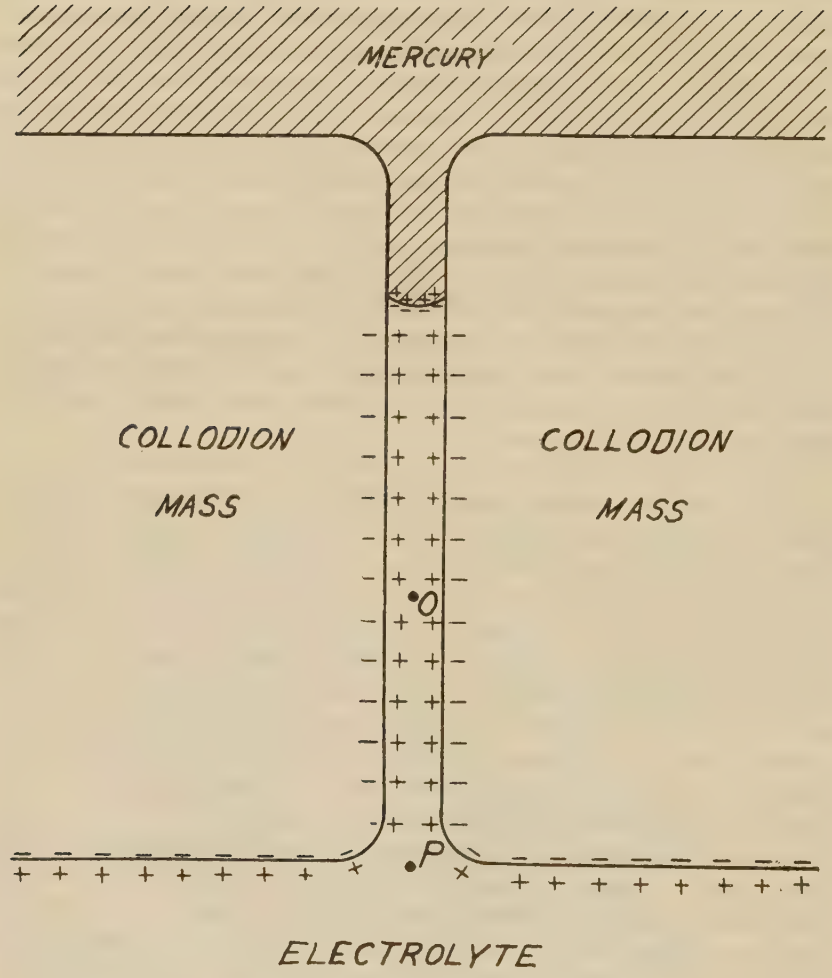
[10] Bartell, F. E., and Van Loo, M.: *J. Phys. Chem*, 38, 161 (1924).

It will be remembered that, in mounting the membranes, hot paraffin was poured into the space P in tube C. Since the membrane covered the hole O, the paraffin did not touch the electrolyte. There are, then, the following contacts in the cell: paraffin|membrane, paraffin|glass, membrane|glass, membrane|electrolyte, glass|electrolyte, mercury|membrane, mercury|glass, and mercury|electrolyte. According to Coehn and Franken (loc. cit.) there is a potential difference at all these contacts, due to differences in dielectric constants. But since the measurements were not made across many of these contacts, not all of them will have an appreciable effect on the readings. The contact with greatest effect on the values read is, of course, the mercury|electrolyte contact. It is only when other influences make the potential differences at this kind of contact in the membrane pores different from that at the same kind of contact at the inner end of the tube K that we get the potential difference which has been called here "specific charge." Of the other contacts, the influence of the membrane|electrolyte contact potential difference is probably the predominating one, although the mercury|membrane contact may also exert an appreciable effect. The other contacts mentioned above should have little effect on a specific charge.

An hypothesis will now be advanced to show how the membrane|electrolyte contact potential difference will influence the equilibrium between Hg^+ ions and the little mercury surfaces in the membrane pores, and thus give rise to a specific charge. Assume that the membrane is charged negatively and that, therefore, the electrolyte side of the double layer is charged positively. This condition is illustrated in Figure 2, which represents one pore of the membrane with the mercury above it and the electrolyte below it, as they were in the cells used. The width of the pore is, however, exaggerated in this figure, for while the actual thickness of the collodion membranes was about 0.22 mm., the diameter of the pores was only of the order of magnitude of a micron.

Around the charges on each side of a double layer are electrical fields. Now it must be remembered that the intensity of an electrical field is inversely proportional to the square of the distance from the charge, and that the two sides of a charged double layer do not coincide, but are spacially separated, although only a very small distance exists between them. Hence any point P, Figure 2, just at the mouth of a pore, is a little closer to the positive charges of the liquid layer than to the negative charges on the collodion mass. Therefore, very close to the end of the pore the positive field from the charges on the liquid side of the double layer predominates to some extent. This must be so, since the distances are small and

FIGURE 2



the positive charges are nearer and would tend to screen off the negative field of the relatively more distant negative charges on the collodion. At larger distances, of course, both fields would neutralize each other, but at these small distances they should not. Hence, if a negative charge were at the point, P, Figure 2, it would be drawn into the pore. But if it were at the point O, there would be no unbalanced electrical fields acting upon it.

Now at the large mercury surface at the inner end of the tube K, in Figure 1, there exists the usual equilibrium between osmotic pressure and the opposing forces of the solution tension of mercury and electrostatic force. At each of the mercury surfaces in the pores of the collodion the same forces are acting. The only difference here is, according to this hypothesis, that the concentration of the electrolyte within the pores must necessarily be different from that in the cell below. This difference arises as follows: When the membranes are first put into the cells, the pores are full of distilled water, but at once diffusion starts, because of osmotic pressure, to equalize the concentrations of solutes within and without the pores. In this case, the solutes are all electrolytes and the ions that diffuse are, of course, charged. As each ion reaches the mouth of a pore, as at point P, Figure 2, it is either drawn inward or repelled outward, according to whether it is negatively or positively charged. Hence when equilibrium is finally reached, the concentration within the pores is not the same as it would be if the pore walls were not charged. That is, the concentration of the Hg^+ ions, in the case assumed, would be less. For this reason, the positive charge at the little mercury surfaces in the pores would not be as great as the charge at the inner end of the tube K in Figure 1. Therefore, when the membrane potential would be read across the cell under these conditions, the membrane would appear to be charged negatively. If, on the contrary, the charge on the collodion mass be assumed to be positive, then the liquid layer would bear a negative charge. Then the Hg^+ ions would be attracted by the predominating negative field, which in this case would aid the osmotic pressure, and the concentration would be greater in the pores than outside. Hence the positive charge on the mercury surfaces in the pores would be greater than on an open surface, and the membrane would appear to be charged positively, when the cell potential difference is measured. Therefore, in either case, the specific charge as read, is the same in sign as the actual charge on the collodion mass, but of course, is different from it in magnitude. In other words, the specific charge as read is only the difference between two single electrode potentials which are different because the concentrations of the ions in contact with the electrodes are different.

This must be so, for the measurements are made through the pores and not across the collodion|electrolyte contact surface. No attempt is made in this dissertation to determine the quantitative relation between the specific charge as read and the actual charge on the membrane.

In the case of other membranes and equilibria in which the action may not take place altogether through holes, but perhaps somewhat through the membrane material, the specific charge must play a more important role. For then it adds more directly to the thermodynamic effect and not indirectly through its effect on another equilibrium.

Specific Charge Data

In order to show the effect of various conditions on the specific charge as read across a collodion membrane in a Des Coudres cell, the temperature was varied first. Table II shows the influence of temperature at zero pressure. In the actual experiments the membranes were never left for any time at zero pressure, for when this was tried some of the electrolyte would seep through the membrane and ruin it for further measurements. A pressure of about 40 cms. of mercury was usually kept on the membranes to prevent this. The values given in Table II were read under these conditions, but are corrected for this pressure by subtracting 1 microvolt for each 5 cms. of mercury. The data in this table were obtained at least two weeks after the cells were set up. After this length of time it was found that the potentials did not usually vary much. The values given are averages of readings for two days, during which time the fluctuations on either side of the average were usually not more than a few microvolts, although at times they were as much as 20 percent of the value given. Since no continued tendency up or down was observed in the two days (or more) it was assumed that equilibrium had been reached.

TABLE II

EFFECT OF TEMPERATURE ON SPECIFIC CHARGE

Temperature	Specific Charge in Microvolts			
°C.	I	II	III	IV
20	+15	+10	+2	+10
25	—74	—100	—40	—30
30	—98	—264	—90	—45

The data given in Columns I and II are from an electrolyte of 0.1 N $HgNO_3$ and 0.02 N HNO_3. This is the weakest acid that will prevent hydrolysis and precipitation of the mercury salt. The two columns give data from two different runs made about a month

apart with membranes from two different sources of collodion. The data in these columns show about the extent to which the results can be duplicated. The electrolyte from which the values in Column III were obtained was 0.1 N with respect to both $HgNO_3$ and HNO_3, while that which Column IV represents was 0.1 N $HgNO_3$ and 0.5 N HNO_3.

According to the above data, the higher the temperature the more negative the specific charge becomes. This general tendency was observed with all the collodion membranes used, except when they were positively charged at 25° C., which happened when the strength of HNO_3 was normal or greater. However, with the HNO_3 normal or stronger, the results obtained were very erratic. A few fluctuating readings from parchment paper and gold beaters' skin membranes indicated that the negative charge dcreased at higher temperatures, as was the case with the collodion membranes in the strong acid electrolytes. Like the four cases shown in Table II, with most of the electrolytes used, a reversal of sign was observed at a temperature a little over 20° C. Little published data on the effect of temperature was found. Coehn and Franken (loc. cit.) found a reversal of sign in the potential difference at the contact surface between paraffin and water. They observed, however, that the paraffin became more positive the higher the temperature.

After equilibrium has been reached at a given temperature, the magnitude and sign of the potential difference between the collodion and the electrolyte must depend on the dielectric constants of the collodion and electrolyte and on the adsorption effects. Under the experimental conditions in this investigation, these two effects oppose each other. That is, from the difference between the dielectric constants, the collodion would be expected to be negatively charged,[11] while in the acid electrolytes used, the absorption of $Hg+$ and H^+ ions, which are more powerful in effect than the NO_3^- ions,[12] would tend to make it positively charged. Hence, both the magnitude and sign of the net potential difference between the collodion membrane and the electrolyte should depend on which factor predominates. Temperature changes should affect these two factors to a different extent. Since the effects are opposing, it is reasonable to suppose that a temperature could be found where the two just balance and the net charge would be zero. For most conditions in this investigation, as stated above, this temperature was found to be a little over 20° C. Therefore, whatever be the other conditions

[11] Coehn and Franken, loc. cit.; Lenard, P.: *Ann. Physik*, 47, 463 (1915); Frankel, J.: *Phil. Mag.* 33, 297 (1917).

[12] Perrin, J., loc. cit.; Bartell and Hooker, loc. cit.

surrounding a membrane, it is certain that its charge will depend also on its temperature.

The change of the specific charge as the composition of the electrolyte is varied is shown in Table III. The various figures as arranged in this table are self explanatory, and are the averages of many runs. The final values were taken at least three weeks and sometimes four weeks after the membranes first touched the electrolytes. The values used for averaging deviated on either side of the figure given about 20 percent as a maximum, with the exception of those for the normal acid, which as stated before, were erratic. The normal acid did, however, always cause the membrane to be charged positively at all temperatures investigated.

TABLE III

EFFECT OF COMPOSITION OF ELECTROLYTE ON SPECIFIC CHARGE AT ZERO PRESSURE AND AT 25° C.

	Composition of Electrolyte in Normalities.					
HNO_3	0.02	0.1	0.5	1.0	0.5	0.5
$HgNO_3$	0.1	0.1	0.1	0.1	0.01	0.5
Specific Charge in Microvolts	—75	—40	—30	+350?	—35	—15

It is evident that varying the concentration of the electrolyte will doubtless change somewhat its dielectric constant. However, the effect on the extent of adsorption is the predominating factor here. This is clearly demonstrated in Table 3. In every instance, the higher the concentration of H^+ or Hg^+ ions, the more positive or less negative is the membrance charge. When high enough, the negative charge which would be on the collodion due to the difference of dielectric constants is overcome and the sign reversed. This agrees with the results of other workers on many different materials.[13]

The changing of the charges over a period of time is shown in the curves in Figures 3 and 4. The curve in Figure 3 is an example of a case in which the final specific charge at equilibrium is negative, whereas in Figure 4 the curve represents the varying charge for conditions such that the final value is positive. Because of the rapid changes, measurements soon after the membrane first touched the electrolyte were hard to make. For this reason the values given for this period are not very accurate, and the curve simply shows the general trend. In all cases, the charge as measured at the start was negative. This is because the pores of the collodion membrane are filled with water at first, and hence the single elec-

[13] Perrin, loc. cit.; Bartell and Hooker loc. cit.; Coehn and Franken, loc. cit.

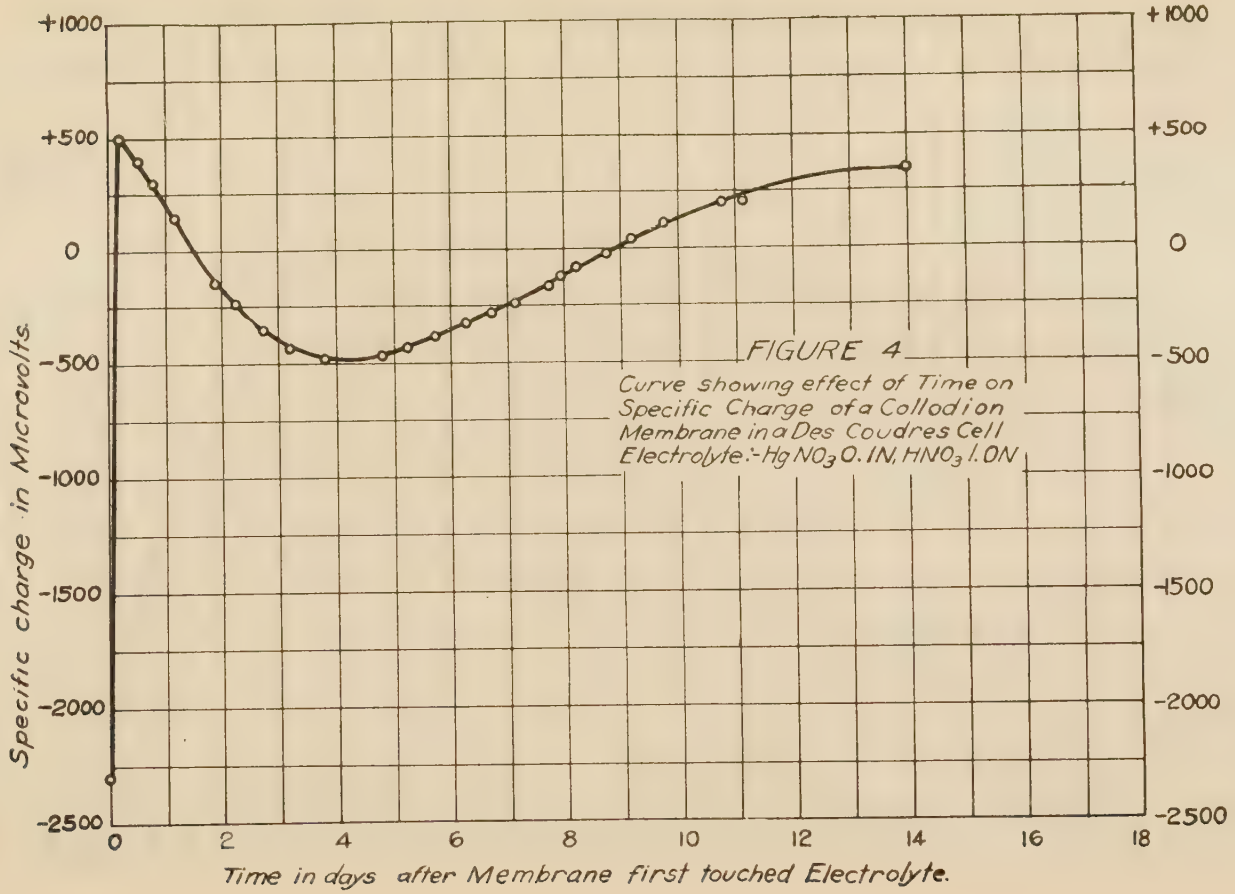


FIGURE 4

Curve showing effect of Time on Specific Charge of a Collodion Membrane in a Des Coudres Cell Electrolyte:- $HgNO_3$ 0.1N, HNO_3 1.0N

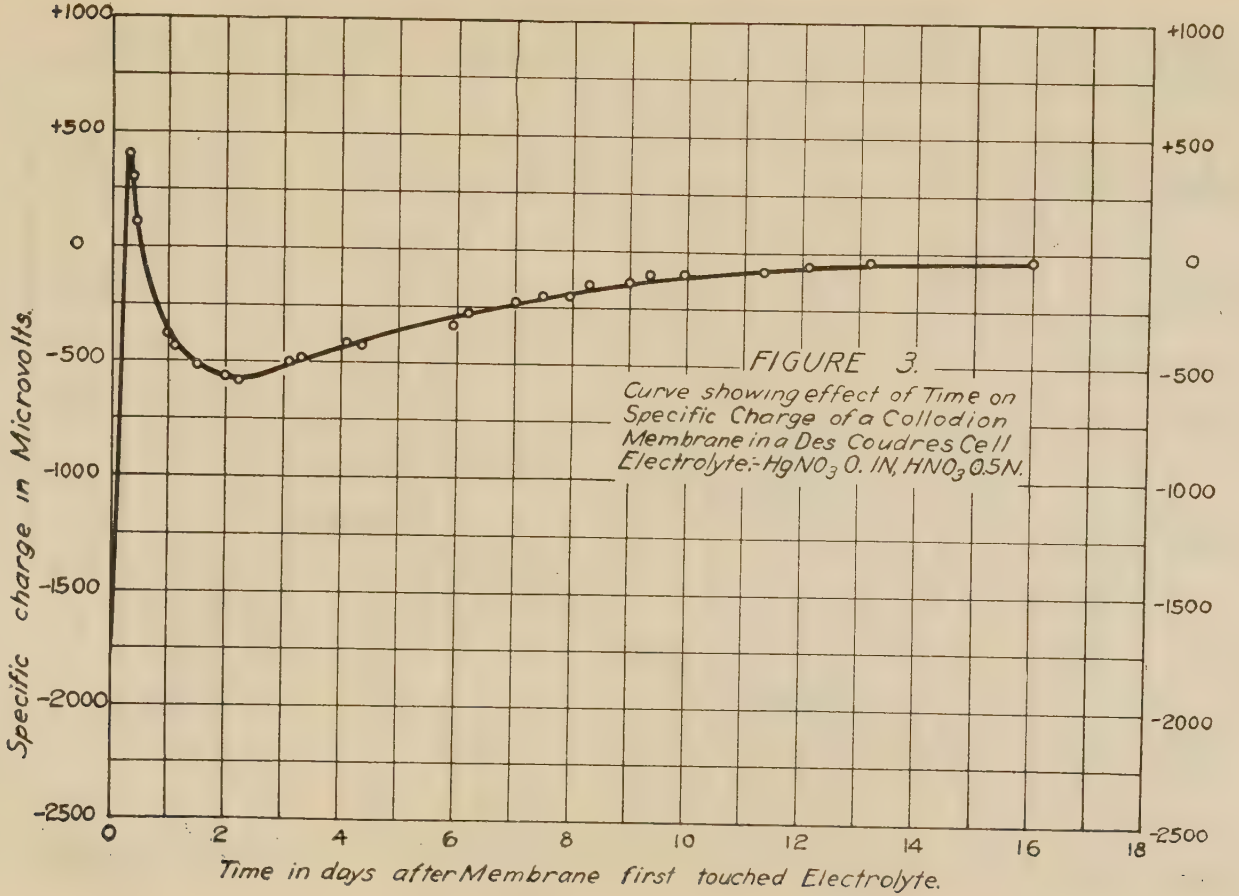


FIGURE 3.

Curve showing effect of Time on Specific Charge of a Collodion Membrane in a Des Coudres Cell Electrolyte:- $HgNO_3$ 0. 1N, HNO_3 0.5N.

trode potential common to all the little mercury surfaces in these pores is not nearly so positive as the single electrode potential of the surface at the inner end of the tube K in Figure 1.

When the membrane comes into contact with the electrolyte, diffusion begins to equalize the composition of the liquid in the pores with that of the electrolyte below them. Because of the fast moving H^+ ions, there is set up a boundary potential which is in opposition to the first mentioned negative effect. Then, also, as the Hg^+ ions diffuse into the pores, they deposit on the mercury surfaces and begin to equalize the two mercury surface potentials. Soon, because of these two latter effects, the sign of the apparent charge is reversed. As the acid concentration becomes equalized within and without the pores, the positive boundary potential decreases. Hence, the curve soon passes through a maximum, begins to fall, and soon again goes through zero. The diffusion of the $HgNO_3$ will, of course, tend to create a boundary potential also, but this effect is masked by the larger one due to the rapidly moving H^+ ion. It is the net boundary potential which helps to bring about this temporary reversal in sign.

When the net boundary potential almost ceases to exist, the curve no longer continues to fall but passes through a minimum, and then rises again. The original negative charge on the collodion mass due to the difference of dielectric constants, has from the start been gradually reduced by adsorption of positive ions. This negative charge has retarded the entrance of Hg^+ ions into the pores, because of the positive field due to the positively charged liquid side of the double layer. Since this influence is now decreasing, more Hg^+ ions can now get into the pores and deposit on the mercury surfaces. Hence the difference between the charge on these surfaces and that on the surface at the inner end of the tube K in Figure 1, is steadily decreasing, and the curve rises towards zero, until equilibrium is reached between the combined effects of the solution tension of mercury, the electrostatic force at the mercury|electrolyte contacts in the pores, and the osmotic pressure of the Hg^+ ions corresponding to the concentration of $HgNO_3$ within the pores, which is modified by the electrical fields of the double layers at the collodion|electrolyte contact, as described in the discussion of the hypothesis above. As the curves show, about two and one-half weeks must elapse after the membrane first touches the electrolyte before the specific charge becomes really constant. The curve in Figure 3 illustrates a case in which the final specific charge at equilibrium is negative. In Figure 4 the final charge represented is positive. All values given in the tables

above were read after the final equilibrium was reached and the curve had become practically horizontal.

As far as could be found, little similar data has been published showing the effect of time on the membrane charge. As stated above, the actual values of the specific charge as read in this cell are not the same as the charges existing on the membranes. These curves do, however, show qualitatively the effect of time on the actual membrane charge. The effect of time on boundary or diffusion potentials has, of course, been observed and recorded before. Lewis and Rupert[14] in working with liquid junctions, found that equilibrium was established in twenty-four hours. They observed a maximum change in potential difference of about 0.8 of a millivolt, without, of course, any reversal in sign. Cumming and Gilchrist[15], in making observations on cotton wool boundaries for twenty-four hour periods, found diffusion to be practically complete in six hours. They recorded no reversal in sign.

In using several kinds of membranes at the boundary A in the following chain

$$\underset{\text{A}}{\text{1.0 N KCL}\,|\,\text{0.1 N HCl}}\,|\,\underset{\text{B}}{\text{1.0 N KCl}}$$

with only the liquid junction at B, they observed in most cases that the potential of the chain fell steadily to zero in twenty-six hours. Lewis and his students[16], using the "Sandfullung" of Bjerrum[17] which was simply a layer of sand in which the two liquids of different concentrations met, found at first the surprisingly high potential difference of 0.03 volt which—"fell rapidly without reaching any definite limiting value." The comparatively high initial potential difference and the rapid fall is similar to the results recorded in this dissertation.

CONCLUSIONS

From the above data and discussions it is evident that the charge on any membrane depends on a number of factors. Temperature, composition of the electrolyte, nature of the membrane, and the period of time after exposing the membrane to the electrolyte, all influence the potential difference between the electroyte and the membrane. For some membranes, this potential difference indi-

[14] Lewis, G. N. and Rupert, F. K.: *J. Am. Chem. Soc.*, 33, 299 (1911).

[15] Cumming, A. C. and Gilchirst, E.: *Trans. Farad. Soc.*, 9, 174, (1913).

[16] Lewis, G. N., Brighton, T. B., and Sebastion, R. L.: *J. Am. Chem. Soc.*, 39, 2245 (1917).

[17] Bjerrum, N.: *Z. Physick. Chem.*, 53, 430 (1905).

rectly influences a membrane potential as read across the membrane. This is the case in a Des Coudres' cell. In this dissertation, the term "specific charge" has been given to the indirect effect of such influence. In other membranes in other equilibria the influence may be direct. That is, the difference between the potential difference at each side of the membrane and the electrolyte may itself be the specific charge. This would be the case if potential measurements were made through the mass of the membrane and not through holes or pores as is done with collodion membranes in a Des Coudres cell.

It has been shown in this work that for a Des Coudres cell, when one attempts to measure thermodynamically calculable membrane potential, the specific charge is always included in the measurements. From some general similarities, it may be inferred that in a Donnan equilibrium a specific charge might also exist. Therefore, in general, in all membrane equilibria, the nature of the membranes and their surrounding conditions should be investigated and their specific charges determined. Otherwise, the results of membrane potential measurements are likely to be meaningless.

SUMMARY

1. An investigation of the Des Coudres cell was made under different conditions.

2. The membranes used in this cell were found to be specifically charged even when no pressure was placed upon them.

3. As the result of specific charges, the membrane potentials as read did not agree with the values calculated from Des Coudres' equation.

4. It was found that within the limits of experimental error, the membrane potentials were the algebraic sum of the specific charges and the calculated values.

5. The effects of temperature, composition of electrolyte, nature of the membrane, and the period of time after exposing the membrane to the electrolyte, on the specific charge of membranes in a Des Coudres cell were studied.

6. In a Des Coudres cell, it was assumed that the actual potential difference between the membrane and electrolyte indirectly affected the membrane potential as read. This indirect effect (the specific charge) was assumed to be due to the action of the electrical field around the charged double layer at the contact surface of electrolyte and membrane. It was assumed that the field of the liquid layer predominated over the field due to the charge on the collodion

mass and aided or opposed the osmotic pressure in its tendency to cause diffusion of the ions into the pores. This was assumed to make the concentrations of electrolytes in the pores different from that without and so cause the single electrode potentials at the surface of mercury in the pores to be different from that at an open surface of mercury. The membrane potentials were read between a number of such surfaces within pores and a large open one and this difference of potential existing at zero pressure was called the "specific charge."

7. If, in other equilibria, the membrane potential measurements were made through the mass of the membrane instead of through holes, the specific charge would be more nearly, if not exactly, the same as the difference between the contact potential differences on the two sides of the membrane.

8. It has been pointed out that the specific charges of the membranes must be taken into consideration in measurements of membrane potentials.

AUTOBIOGRAPHY

I, John Mouk Ort, was born at Home City, Ohio, May 31st, 1896. I received all of my secondary school education in the public and high schools in the village of Osborn, Ohio, and in a nearby country school. My undergraduate education was obtained at The Ohio State University, from which I received the degree of Bachelor of Chemical Engineering in 1918 and the degree of Master of Science in 1919. From 1919 to 1922 I was an Instructor in Chemistry at Case School of Applied Science. In 1924 I received from The Ohio State University the degree of Doctor of Philosophy, after a two years' residence, the last year as the duPont Fellow in Chemistry.

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